CHEMICAL EQUILIBRIUM MIXTURE COMPUTATIONS FOR ENERGETIC MATERIAL COMBUSTION IN CLOSED VESSELS

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ABSTRACT

A major computational code called CERV was developed to determine complex equilibrium compositions of a nonideal mixture of numerous imperfect gases and compressible liquid and solid species with phase transitions for closed-vessel applications. This code minimizes Gibbs energy using reaction variables, in contrast to other major codes like BRL-Blake, BRC-Bagheera and NASA-CEA that use composition variables such as mole numbers. The CERV code has significant advantages in handling compressible condensed species with phase transitions and computing nonideal mixture compositions accurately and efficiently. Computations are done robustly, without convergence failures from matrix inversions or iterative procedures, for problems with reaction products consisting of hundreds of gaseous, liquid and solid species.

1. INTRODUCTION

A thorough knowledge of chemical equilibrium mixture compositions and thermodynamic properties of the reaction products of energetic materials is important not only in the design, performance analysis and utilization of engineering equipment such as compressors, turbines, heat exchangers, combustion engines, shock tubes, rockets and projectile launchers, but also in the formulation and characterization of energetic materials such as fuel-air mixtures, propellants, explosives, primers, fuses and igniters. The equilibrium-mixture composition (i.e., types of gaseous, liquid and solid species in the reaction products and their mole numbers) and its thermodynamic properties (e.g., pressure, volume, temperature, internal energy, Gibbs energy) are normally not available from measurements or experiments, so they are predicted instead by using computational methods based on appropriate models for the chemical activity, type of mixture (ideal or nonideal) and pressure-volume-temperature properties (equation of state) of the gaseous, liquid and solid species. The benefits of the computational methods in providing accurate predictions for the applications mentioned previously depend considerably on the physical validity and completeness of the underlying models.

The challenges of providing a thorough knowledge of chemical equilibrium mixture compositions, thermodynamic properties and models are being met by advancements in chemical equilibrium theory, modelling and solution methods and by developments in computer algorithms. Although ideal and nonideal mixture models are well developed, advancements are required for more accurate equations of state and additional thermochemical data for imperfect gas behaviour and for the compressibility of liquids and solids. This paper illustrates the capabilities and advantages of a new computational code (CERV) in solving combustion problems involving energetic materials by using present-day models for ideal and nonideal mixtures, for equations of state for perfect and imperfect gases, and for liquid-solid and solid-solid phase transitions.

2. MAJOR COMPUTATIONAL CODES

The NASA-CEA code was developed at the NASA Lewis Research Center in the United States (US) over the past 50 years to solve combustion-product compositions and thermodynamic properties associated with energetic materials, rocket engines and shock waves and detonations in gases for the US aerospace and military programs. This code is based on an ideal mixture model, an equation of state (EOS) for perfect gases, and condensed species that have no volume in the reaction products. The Blake code was developed in the 1970s and 1980s at the Ballistic Research Laboratory of the US Army for military applications involving propellants, explosives, primers, fuses and igniters. Because the pressures and densities of the reactant-product mixtures for such applications are generally high, the Blake code is based on a nonideal mixture model, an EOS for imperfect gases (e.g., virial EOS), and compressible condensed species that have finite volumes. The Bagheera code was developed in the 1980s and 1990s in France for similar purposes, and it is based on an ideal mixture model, a modified virial EOS and includes the volumes of condensed species. By the early 1990s the Bagheera code supplanted the Blake code as the standard for military applications in NATO countries. See Wong, Gottlieb and Lussier (2003) for a more detailed review of these codes.

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The CERV code was developed in the 1990s at the University of Toronto in Canada, starting with the doctoral studies of F.C.H. Wong (2001), for solving fairly general chemical equilibrium problems, but with emphasis on energetic material combustion in closed vessels for military applications. This code has the capability of using either ideal or nonideal mixture models, different EOS for perfect and imperfect gases and either incompressible or compressible condensed species. This code is based on the earlier work of Villars (1959, 1960), Cruise (1964), Smith and Missen (1967, 1968), who solved problems for a specified mixture temperature and pressure and using the simplest ideal mixture of perfect gases and condensed species without volume. Smith and Missen used the name VCS method; we use the acronym CERV stemming from chemical equilibrium using reaction variables.

The essential capabilities of the NASA-CEA, Blake, Bagheera and CERV codes are summarized in Table 1. Most of these codes can solve the two basic problems of a specified equilibrium-mixture temperature and pressure (T-P problem) and a specified energy and volume (E-V or closed-vessel problem). If individual volumes of condensed species are ignored, then the modelling of condensed species as incompressible or compressible is irrelevant or not applicable (NA). Some codes are used with well-known equations of state stemming from Redlich, Kwong and Soave (RKS); Benedict, Webb, Rubin, Starling and Han (BWRSH); Becker, Kistiakowski and Wilson (BKW);

and Powell, Wilmot, Haar and Klein (PWHK). See Wong, Gottlieb and Lussier (2003) for details and references on these EOS and the virial EOS.

3. BNR AND CERV SOLUTION METHODS

The NASA-CEA, Blake and Bagheera codes determine equilibrium-mixture compositions for T-P and E-V problems by minimizing the Gibbs or Helmholtz energy of a mixture using composition variables (mole numbers). The Gibbs energy $G(\boldsymbol{n})$, where $\boldsymbol{n}$ denotes all gaseous and condensed species mole numbers (numbering N_s), is minimized subject to mass conservation constraints on atomic elements that are included explicitly by means of a set of Lagrange constraint multipliers $\boldsymbol{\lambda}$, one for each atomic element (numbering N_e) in the reactants. This results in the Lagrangian $L(\boldsymbol{n}, \boldsymbol{\lambda}) = G(\boldsymbol{n}) - \sum_{i=1}^{N_e} \lambda_i \left(a_i - \sum_{j=1}^{N_s} F_{ij} n_j \right)$, where a_i are the entries of an atomic element abundance vector $\boldsymbol{a}$, and F_{ij} are the entries of a molecular formula matrix $\boldsymbol{F}$. The minimization of $L(\boldsymbol{n}, \boldsymbol{\lambda})$ yields the minimum of $G(\boldsymbol{n})$ and the equilibrium composition $\boldsymbol{n}$.

Several solution methods have been developed for minimizing $L(\boldsymbol{n}, \boldsymbol{\lambda})$. The most renown are the Brinkley, NASA and RAND Corporation methods, referred to collectively as the BNR methods, which stem respectively from the work of Brinkley (1947); Huff, Gordon and Morrell (1951); and White, Johnson and Dantzig (1958). In BNR methods, an appropriate set of gaseous, liquid and solid species is selected as reaction products, their mole numbers are estimated, and an iterative procedure (second-order Newton-Raphson scheme) is used to descend step by step to the minimum of $L(\boldsymbol{n}, \boldsymbol{\lambda})$. At each step along the descent path a set of linear equations of the form $\boldsymbol{A}\Delta\boldsymbol{x} = \boldsymbol{b}$ must be solved to yield $\Delta\boldsymbol{x} = \boldsymbol{A}^{-1}\boldsymbol{b}$, where $\Delta\boldsymbol{x}$ denotes corrections to both $\boldsymbol{n}$ and $\boldsymbol{\lambda}$ from the previous step. Matrix $\boldsymbol{A}$ must be invertible (nonsingular) or a convergence failure will occur before $\Delta\boldsymbol{x}$ can be evaluated.

The minimization problem for BNR methods must be posed carefully to avoid theoretical singularities in matrix $\boldsymbol{A}$. For example, the initial selection of gaseous and condensed species must not include two condensed species with the same molecular formula such as liquid water and ice, and the phase rule must be satisfied by restricting the number of condensed species in the reaction products (normally to one less than the number of atomic elements N_e). Even when matrix $\boldsymbol{A}$ is theoretically invertible (nonsingular), it can become ill-conditioned or numerically singular during computations from number round-off errors, and thereby result in a convergence failure. This situation worsens dramatically as the mass content of the gaseous species diminishes significantly relative to that of the condensed species, a frequent occurrence in solving T-P and E-V problems involving primers, fuses and igniters.

The most advanced and popular BNR methods described by Gordon and McBride (1994) contain a

Table 1. Capabilities of major computational codes.

feature \ code	CEA	Blake	Bagheera	CERV
T-P problem	yes	yes	no	yes
E-V problem	yes	yes	yes	yes
ideal mixture, perfect gases	yes[1]	yes[1]	yes[1]	yes[1]
ideal mixture, imperfect gases	no	no	yes[2]	yes[2,3]
nonideal mixture, imperfect gases	no	yes[4]	no	yes[3]
one phase for all gaseous species	yes	yes	yes	yes
one phase for each condensed species	yes	yes	yes	yes
volumes of condensed species	no	yes	yes	yes
incompressible condensed species	NA	yes	yes	yes
compressible condensed species	NA	yes	no	yes
phase transitions	yes	yes	yes	yes
different densities for two species in phase transition	NA	yes	no	yes

[1]EOS for perfect gases   [3]virial, RKS, BWRSH EOS
[2]modified virial EOS   [4]virial, BWK, PWHK EOS

multiple-loop iterative scheme, which is embedded in the NASA-CEA code and emulated in the Bagheera code. To avoid theoretical matrix singularities and phase-rule violations, the initial reaction products for T-P and E-V problems are selected as gaseous species only and their mole numbers are estimated (e.g., each is one mole divided by the number of gaseous species). $L(\boldsymbol{n}, \boldsymbol{\lambda})$ and thereby $G(\boldsymbol{n})$ are minimized iteratively to determine the corresponding equilibrium composition $\boldsymbol{n}$, which is the first iterative loop. One condensed species is possibly introduced into the mixture, on the basis of a specialized checking procedure, such that it is the condensed species not included in the mixture that should lower $L(\boldsymbol{n}, \boldsymbol{\lambda})$ the most if added to the mixture. Then $L(\boldsymbol{n}, \boldsymbol{\lambda})$ is minimized again with the additional condensed species (initial mole number of zero), to perform the second iterative loop. If any condensed species included in the mixture has a negative mole number, it is removed from the mixture. If another condensed species not included in the mixture should be included, this is done, and another iterative loop is performed. This looping ends and the final equilibrium composition $\boldsymbol{n}$ is obtained when condensed species are neither removed nor added to the mixture.

The iterative procedure in BNR methods is an inefficient multiple-loop structure that cannot be reduced to a single loop, because the specialized checking procedure for condensed species is based on using equilibrium mixture conditions that are established only at the end of an iterative loop. In the NASA-CEA and Bagheera codes the variables $\ln(n_i)$ are used instead of n_i for the gaseous species only, which has the important advantage of making all gaseous mole numbers nonnegative during the iterative procedure.

The CERV method and code determine the equilibrium mixture composition for a T-P problem by minimizing the Gibbs energy $G(\boldsymbol{\xi})$ expressed in terms of reaction variables or stoichiometric-vector multipliers $\boldsymbol{\xi}$, numbering $N_{\mathrm{r}} = N_{\mathrm{s}} - N_{\mathrm{e}}$ instead of $N_{\mathrm{s}} + N_{\mathrm{e}}$ composition variables and Lagrange constraint multipliers. The reaction variables are related to the composition variables by the linear transformation $\boldsymbol{n} = \boldsymbol{n}^* + \boldsymbol{N}\boldsymbol{\xi}$, where $\boldsymbol{n}^*$ is a known set of mole numbers (e.g., initial guesses) and $\boldsymbol{N}$ is a special $N_{\mathrm{s}} \times N_{\mathrm{r}}$ matrix of stoichiometric coefficients. The mass conservation constraints on the atomic elements ($\boldsymbol{F}\boldsymbol{n} = \boldsymbol{a}$) are integrated directly into the formulation by means of matrix $\boldsymbol{N}$, and each column of $\boldsymbol{N}$ is a set of stoichiometric coefficients associated with a particular chemical reaction occurring among some gaseous and condensed species.

The minimum of $G(\boldsymbol{\xi})$ and corresponding equilibrium composition $\boldsymbol{n}$ are obtained iteratively by using a standard second-order variation scheme. An appropriate set of gaseous, liquid and solid species is selected as reaction products, and their mole numbers are estimated by using linearization and the well-known simplex method that ensures the mass conservation con-

straints are satisfied. A quadratic approximation $Q(\boldsymbol{\xi})$ to $G(\boldsymbol{\xi})$ is constructed in terms of $\boldsymbol{\xi}$, by matching the two functions in terms of $\boldsymbol{n}$ and first derivatives of $G(\boldsymbol{\xi})$ with respect to $\boldsymbol{\xi}$. Finding the minimum of $Q(\boldsymbol{\xi})$ leads to a set of N_{r} linear equations of the form $\boldsymbol{H}\Delta\boldsymbol{\xi} = \boldsymbol{c}$, in which $\boldsymbol{H}$ is a $N_{\mathrm{r}} \times N_{\mathrm{r}}$ Hessian matrix. In the CERV method the Hessian matrix is made diagonally dominant because of the special form of matrix $\boldsymbol{N}$. The off-diagonal elements are neglected, the approximate inverse $\boldsymbol{H}^{-1}$ is obtained easily and efficiently by inverting N_{r} scalar and nonzero diagonal numbers, the solutions $\Delta\boldsymbol{\xi} = \boldsymbol{H}^{-1}\boldsymbol{c}$ and $\Delta\boldsymbol{n} = \boldsymbol{N}\Delta\boldsymbol{\xi}$ are calculated, and then $\boldsymbol{\xi} = \boldsymbol{\xi}^* + \Delta\boldsymbol{\xi}$ and $\boldsymbol{n} = \boldsymbol{n}^* + \Delta\boldsymbol{n}$ are obtained for the minimum of $Q(\boldsymbol{\xi})$. The new values $\boldsymbol{\xi}$ and $\boldsymbol{n}$ are closer than the old ones $\boldsymbol{\xi}^*$ and $\boldsymbol{n}^*$ to those that define the minimum of $G(\boldsymbol{\xi})$. Repetition of the quadratic procedure produces a step-by-step descent path to the minimum of $G(\boldsymbol{\xi})$ and a converged solution for the equilibrium composition $\boldsymbol{n}$. See the book by Smith and Missen (1991) and the report by Wong, Gottlieb and Lussier (2003) for more details on the minimization procedure and CERV method.

Owing to the reaction-variable formulation of the CERV method, the associated computer code does not suffer convergence failures. The method also features

Table 2. Comparison of BNR and CERV methods for T-P problems.

feature \ method	BNR	CERV
solution method	minimize $L(\boldsymbol{n}, \boldsymbol{\lambda})$ by Newton Raphson scheme	minimize $G(\boldsymbol{\xi})$ by second variation scheme
variables	$\boldsymbol{n}$ or $\ln(\boldsymbol{n})$, $\boldsymbol{\lambda}$	$\boldsymbol{\xi}$, $\boldsymbol{n}$
equations	$N_{\mathrm{s}} + N_{\mathrm{e}}$	$N_{\mathrm{s}} - N_{\mathrm{e}}$
iteration type	multiple loop	single loop
mass conservation of atomic elements ($\boldsymbol{F}\boldsymbol{n} = \boldsymbol{a}$)	side constraint using $\boldsymbol{\lambda}$	embedded constraint in $\boldsymbol{n} = \boldsymbol{n}^* + \boldsymbol{N}\boldsymbol{\xi}$
mass conservation satisfied every step	no	yes
equilibrium equation	$\boldsymbol{\mu} - \boldsymbol{F}^T\boldsymbol{\lambda} = 0$	$\boldsymbol{N}^T\boldsymbol{\mu} = 0$
equilibrium equation satisfied every step	yes — Brinkley no — NASA no — RAND	no
nonnegativity constraint	handled very easily	handled easily
chemical reaction equations included	no	yes
add and remove condensed species	once per loop, reconstruct $\boldsymbol{F}$	once per step, reconstruct $\boldsymbol{N}$
theoretically singular matrix that causes convergence failure	must avoid at outset	NA
numerically singular matrix that causes convergence failure	possible	NA
convergence enforcer	yes	yes
computational speed	good	faster

an efficient single-loop iterative structure, because condensed species can be removed from or added to the reaction products at each step along the single descent path, because the mass constraints are satisfied at each step of the single loop and because the specialized checking procedure is based on species chemical reactions that are embedded in matrix $\boldsymbol{N}$ (rather than on equilibrium conditions as in BNR methods).

The essential features of BNR and CERV methods for solving T-P problems are given in Table 2. These results highlight method similarities and differences, and some major advantages of the CERV method and code. The robustness of the CERV code in not suffering convergence failure is especially important in military applications involving primers, fuses and igniters. The single-loop iterative structure combined with the simple and quick Hessian matrix inversion result in the most efficient computations for equilibrium reaction products modelled as nonideal solutions of imperfect gases and compressible condensed species.

4. COMPUTATIONAL RESULTS

4.1 *E-V* Problem for PETN

The problem of the detonation of pentaerythritol tetranitrate (PETN) in a closed vessel with atmospheric air (298.15 K, 101.325 kPa) surrounding the charge is solved by the CERV code. The final equilibrium temperature, pressure and mixture composition are determined iteratively by repeatedly solving a T-P problem and systematically adjusting the mixture temperature while updating the mixture pressure based on the known closed-vessel volume at each iterative step until the final energy of the reaction products equals the known initial energy of the three reactants $C_5H_8N_4O_{12}$, N_2 and O_2. Other ingredients of air such as Ar and CO_2 are small and ignored, and the ignition source for PETN is neglected.

The computations are done for closed-vessel loading densities δ varying from 0.01 to 0.20 gm/cm^3, where δ denotes the mass of PETN divided by the vessel volume. Results are shown in Figs. 1 and 2 for the cases of a nonideal mixture model and four different equations of state. When the nonideal mixture model is combined with the simplest EOS given by $Pv = \mathcal{R}T$ for perfect gases (PG), the model for the nonideal mixture reduces to that for an ideal mixture of perfect gases, and this serves as a good reference.

The equilibrium mixture pressure P for the case of a perfect gas increases almost linearly with increasing vessel loading density, as shown in Fig. 1, illustrating that T/v also increases linearly with loading density. The pressure variations for the cases of the other EOS all rise more rapidly; this steeper rise stems primarily from the effects of co-volume (stronger intermolecular repulsion forces for larger gas densities). The equilibrium mixture temperature T shown in Fig. 1 features an initial rapid increase for loading densities be-
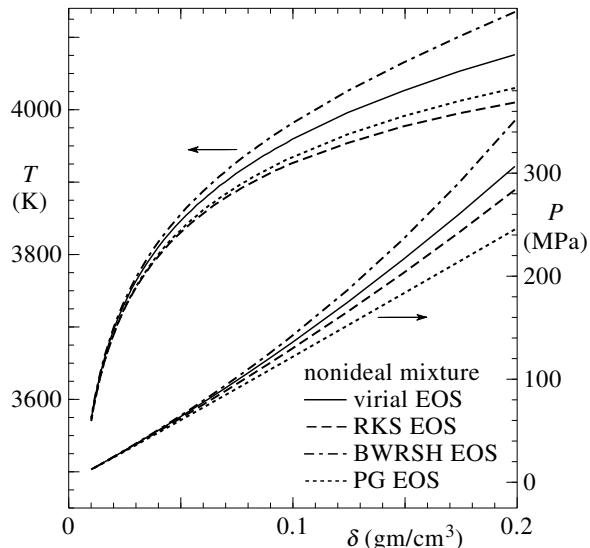

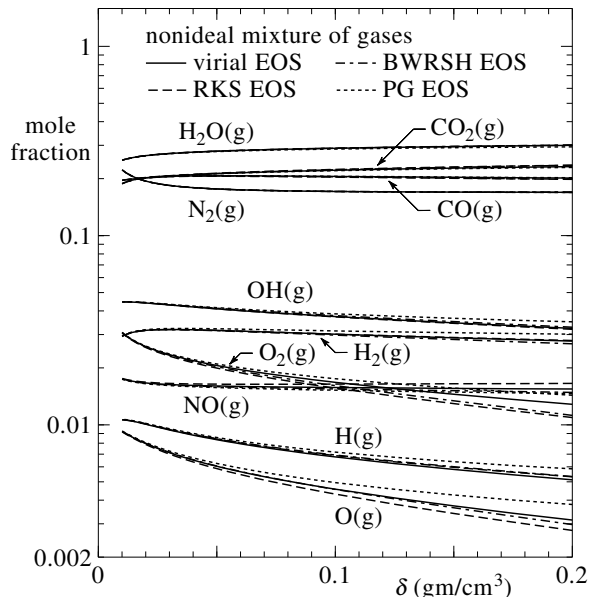Figure 1: Equilibrium temperature and pressure for the detonation of PETN in a closed vessel.

Figure 2: Equilibrium mole fractions for the detonation of PETN in a closed vessel.

low 0.05 gm/cm^3, but this initial rapid rise levels off quickly and appears to approach a maximum temperature asymptotically. The temperature should trend toward a constant adiabatic flame temperature as the loading density increases, or as this temperature becomes less sensitive to an increasing loading density.

The most abundant reaction products for this closed-vessel problem are the gaseous species H_2O, CO_2, CO, N_2, OH, H_2, O_2, NO, H, and O, and their mole fractions are shown in Fig.2, although many other gaseous species such as CH_4, NO_2, N_2O and N are included in the computations. For the combination of atomic elements C, H, N and O of the reactants, the

possible condensed species are C(s-gr), H_2O(liquid) and H_2O(solid). The abundance of graphite was negligible, and liquid water and ice do not exist at the high equilibrium-mixture temperatures for this problem.

The species mole fractions shown in Fig. 2 do not appear to be influenced greatly by the four different EOS, but nontrivial changes are obscured by the logarithmic scale. The maximum differences are 2.3, 2.7, 2.0, 0.5 and 31% among the H_2O, CO_2, CO, N_2 and O_2 data, respectively, at $\delta = 0.20 \, \mathrm{gm/cm^3}$.

4.2 T-P Problem with Solid or Liquid Species

A T-P problem is formulated from the reactants that are composed of the four atomic elements C, K, O and S. The reactants are taken as the ten gaseous species CO_2, CO, SO_2, K, SO, O_2, S, C, K_2SO_4 and K_2, each in the amount of one mole, and the four condensed species as K_2SO_4(s), K_2SO_4(lq), K_2CO_3(s) and K_2CO_3(lq), each in the amount of one tenth of a mole. Equilibrium-mixture compositions are computed by the CERV code for a specified mixture pressure $P = 100$ kPa (1 bar) and two specified mixture temperatures $T = 700$ and 1500 K. The two sets of computed results are shown in the bar chart in Fig. 3, in which the gaseous species are grouped at the top and the condensed species are assembled at the bottom. Note that virtually identical results are obtained for computations based on an ideal or a nonideal mixture of perfect or imperfect gases because the equilibrium-mixture pressure is relatively low for this problem.

The gaseous species CO, S, SO, CO_2 and SO_2 occur in abundance larger than 10^{-6} moles at both temperatures of 700 and 1500 K. However, at 700 K the amounts of the gaseous species K, K_2SO_4 and K_2 are sm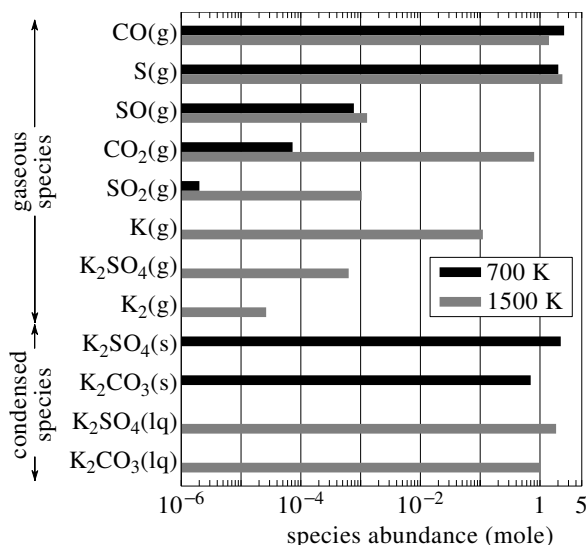aller than 10^{-6} moles, and the two sub-stances potassium sulphate K_2SO_4 and potassium carbonate K_2CO_3 occur as solid species in large amounts, whereas their liquid counterparts are nonexistent. At 1500 K the gaseous species K, K_2SO_4 and K_2 occur in more significant amounts and the two substances K_2SO_4 and K_2CO_3 now exist as liquid species only. This illustrates that large changes in the equilibrium mixture temperature can result in large changes in the amounts of some gaseous species, and some substances can change in form from solid to liquid species.

For this particular T-P problem the species in the reaction products are arbitrarily taken as identical to those in the reactants. The mole numbers of all reactant species are specified at the outset. The initial set of mole numbers of the reaction-product species can be estimated as mentioned previously by using the linearization and simplex method, or they can be taken simply as equal to those of the reactants because the reactant and reaction-product species are identical. This T-P problem is solved both ways by the CERV code, and the final results for the two temperatures shown in Fig. 3 are the same, as might be expected.

This exercise helps demonstrate that the CERV method and code can handle multiple species with the same chemical formula (i.e., liquid and solid forms of substances K_2SO_4 and K_2CO_3) as part of the reaction products, and only the naturally occurring form of a substance will exist in the final equilibrium mixture. This type of input cannot be used by codes based on the BNR method, because matrix $\boldsymbol{A}$ would be theoretically singular and produce a convergence failure.

4.3 E-V Problem with Solid-Liquid Transition

The black powder for this closed-vessel problem is taken as composed by weight of 45% solid potassium nitrate (KNO_3), 23% solid susquehanna charcoal ($C_{1321}H_{573}S_6N_4O_{100}$), 17% solid sulphur (S), 0.5% liquid water (H_2O) and 14.5% solid ash or potassium carbonate (K_2CO_3) at 298.15 K and 101.325 kPa. The reactants with the six atomic elements C, H, K, N, O and S involve 156 gaseous species, 29 condensed species and 12 pairs with possible phase transitions between condensed species of the same substance. For demonstration we select the melting of solid potassium sulphide K_2S(s-3) to liquid K_2S(lq) as the phase transition pair, with a melting temperature $T_{\mathrm{melt}} = 1222.24$ K.

The equilibrium-mixture temperature T, pressure P and composition $\boldsymbol{n}$ are computed by the CERV code for the closed-vessel loading density δ, mass of the black powder divided by the vessel volume, varying from 0.096 to 0.105 $\mathrm{gm/cm^3}$. Some computed results are presented in Fig. 4. For loading densities from 0.096 to 0.09726 $\mathrm{gm/cm^3}$ the mixture pressure and temperature increase, and only the solid phase K_2S(s-3) of potassium sulphide occurs in the mixture. For $0.09726 \leq \delta \leq 0.10377 \, \mathrm{gm/cm^3}$ the mixture temperature remains fixed at the melting temperature

Figure 3: Mole numbers of gaseous and condensed species for a mixture at $P = 100$ kPa and $T = 700$ and 1500 K.
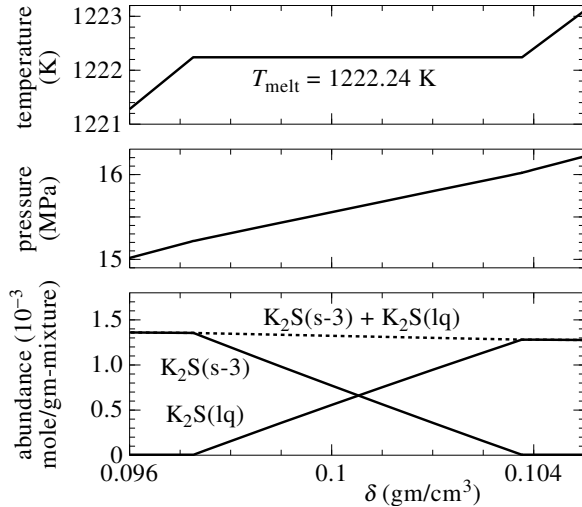
Figure 4: Combustion of black powder in a closed vessel with the melting of potassium sulphide.

1222.24 K, the mixture pressure continues to increase, the amount of the solid phase $K_2S(s\text{-}3)$ diminishes toward zero, and the amount of the liquid phase $K_2S(lq)$ increases from zero as melting continues. The solid phase disappears at the end of this range and only the liquid phase exists afterwards. For loading densities larger than 0.10377 gm/cm^3 the mixture temperature increases once again, along with the mixture pressure.

4.4 T-P Problem with Condensation

Consider a mixture of inert nitrogen N_2, benzene C_6H_6 and toluene C_7H_8 at a specified mixture temperature and range of mixture pressures such that the benzene and toluene can occur in gaseous and liquid forms. The reactants are one-half mole of gaseous nitrogen and one mole each of gaseous benzene and toluene. The mixture composition $\boldsymbol{n}$ is calculated by the CERV code for the reaction products $N_2(g)$, $C_6H_6(g)$, $C_7H_8(g)$, $C_6H_6(lq)$ and $C_7H_8(lq)$, for a specified mixture temperature $T = 298.15$K and pressure P ranging from 5 to 30 kPa. Computed results are shown in Fig. 5, along with the partial pressures $p_{C_6H_6(g)}$ and $p_{C_7H_8(g)}$ of gaseous benzene and toluene. The vapour pressures 12.7 and 3.78 kPa of benzene and toluene, respectively, are also indicated in the figure.

Only gaseous nitrogen, benzene and toluene occur in the equilibrium mixture at mixture pressures below 9.50 kPa. At the mixture pressure of 9.50 kPa the gaseous toluene begins to condense into liquid toluene, and this condensation continues with increasing mixture pressure, resulting in a decrease in the abundance of gaseous C_7H_8 and a corresponding increase in the amount of liquid C_7H_8. At the mixture pressure of 22.85 kPa the condensation of gaseous benzene into liquid benzene begins, and this condensation continues as the mixture pressure increases.

When the chemical potential $\mu_i^g(x_i, T, P)$ of the gaseous species, calculated on the basis of the gaseous
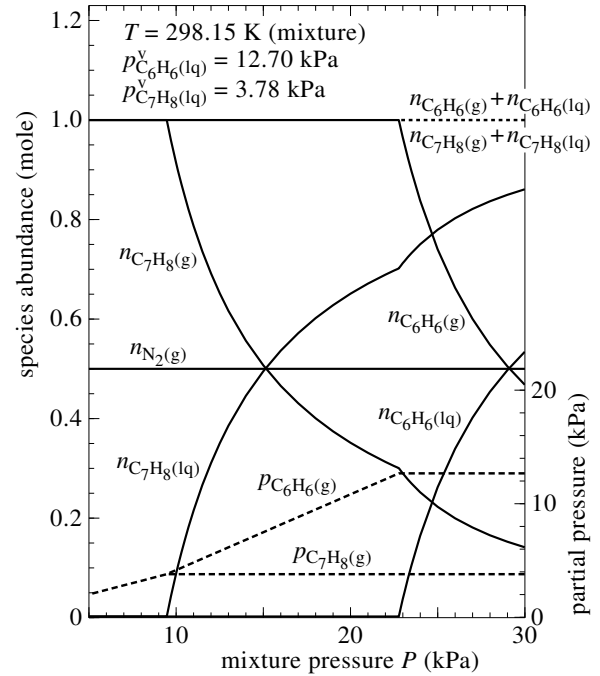

Figure 5: Condensation of benzene and toluene.

mole fraction x_i and mixture temperature T and pressure P, is less than the chemical potential $\mu_j^{lq}(p_j^v, T, P)$ of the related liquid species, calculated on the basis of its vapour pressure p_j^v and mixture temperature T and pressure P, then only the gaseous species exist in the mixture. When these two chemical potentials just become equal, as the mixture pressure increases, condensation just begins. For higher mixture pressures the condensation continues, and the relative amounts of these gaseous and liquid species are determined partly on the basis of $\mu_i^g(x_i, P) = \mu_j^{lq}(p_j^v, P)$. For an ideal mixture of perfect gases and a simplified liquid model, these general relationships reduce to using the partial pressure of the gaseous species $p_i = x_i P$ instead of $\mu_i^g(x_i, P)$ and the vapour pressure of the liquid p_j^v instead of $\mu_j^{lq}(p_j^v, P)$. For this problem with low mixture pressures and densities, these simplified results are sufficient to explain the results shown in Fig. 5.

4.5 E-V Problem with Compressible Species

The black powder in the closed vessel is composed by weight of 69% solid potassium nitrate KNO_3, 25% solid graphite $C(s\text{-}gr)$ and 6% solid sulphur S. These reactants are initially surrounded by air (79% N_2 and 21% O_2) at 298.15 K and 101.325 kPa. The reaction products composed of the six atomic elements C, H, K, N, O and S once again involve 156 gaseous species, 29 condensed species and 12 pairs with possible phase transitions between condensed species of the same substance. The most abundant gaseous species in this problem are CO, N_2, CO_2 KCN, K, COS, $K_2C_2N_2$, K_2CO_3, CS_2, K_2, S_2, CS, SO_2, SO and S_2O. These gaseous reaction products are modelled

as a nonideal mixture of imperfect gases by using a three-term truncated virial equation of state. The condensed species that occur in the equilibrium mixture are solid graphite C(s-gr), liquid potassium carbonate K_2CO_3(lq) and liquid potassium sulphide K_2S(lq).

Compressibility effects of condensed species are illustrated by CERV computations with three compressibility models. The simplest *no-volume* model (used in the NASA-CEA code) includes the mass and energy of the condensed species but neglects their volume (i.e., material density is infinite). The *constant-volume* or *incompressibility* model (used in the Bagheera code) includes the mass and energy of the condensed species with a constant volume and density evaluated for either the solid or liquid that exists at the initial temperature and pressure of the reactants in the closed vessel. The *variable-volume* or *compressibility* model (used in the Blake code) incorporates an approximate pressure-volume-temperature equation of state to include the counter-acting effects of thermal expansion and pressurized contraction on the condensed species at high mixture temperatures and pressures. Equations of state for compressible condensed species were adopted from the Blake-code library.

Computational results for the equilibrium-mixture temperature and pressure are presented in Fig. 6. The lowest mixture temperatures and pressures occur for condensed species with no volume, because this leaves more volume for the gaseous species to occupy at a lower mixture pressure. For constant-volume or incompressible condensed species the mixture temperature and pressure increase by 0.2% and 5.9%, respectively, at $\delta = 0.20$ gm/cm^3. The condensed-species volume reduces the volume available to the gaseous species, which has only a small effect on the mixture temperature but an impact on the mixture pressure.
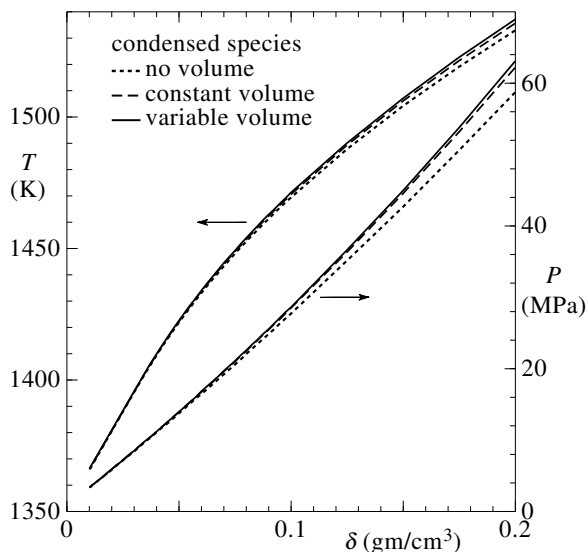

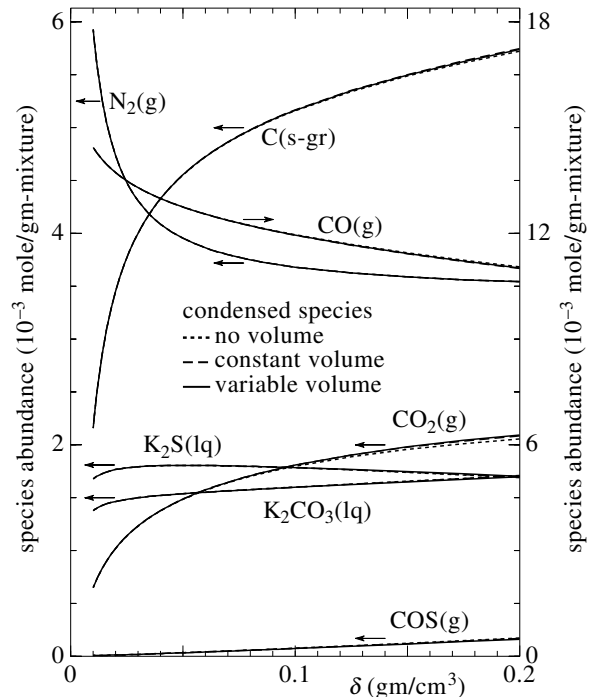Figure 6: Volume effects of condensed species on equilibrium-mixture temperatures and pressures.

Figure 7: Volume effects of condensed species on equilibrium-mixture species abundances.

sure. For variable-volume or compressible condensed species the mixture temperature and pressure are the highest, being 0.3% and 7.4% larger than for the no-volume model. The increase in mixture pressure from changing from constant- to variable-volume condensed species stems mainly from the large thermal expansion of species material at high mixture temperatures, which is only partly off-set by the species-material compression at high mixture pressures, yielding overall a smaller volume available to the gaseous species that gives a higher mixture pressure. The mixture temperature is insensitive to the three compressibility models because the mass and energy of the condensed species are included in all three models.

The effects of compressibility on the gaseous and condensed-species abundances are presented in Fig. 7. The maximum changes in abundances among the three compressibility models at a loading density of 0.20 gm/cm^3 are 1.8% for CO_2, 0.7% for K_2S(lq), 0.5% for K_2CO_3(lq), 0.4% for CO and C(s-gr), 7.6% for COS and 0% for N_2. These effects on the most abundant gaseous and condensed species are therefore quite small. Note that carbon monoxide (CO) is the most abundant species by a factor of about two to six, and its abundance only is given by the larger scale.

5. CONCLUDING REMARKS

Major computational codes called NASA-CEA, Blake, Bagheera and CERV and their solution methods were described to highlight their capabilities in solving civilian and military problems associated with engineering and energetic-materials applications, and

also to illustrate that modern codes need to solve closed-vessel problems without convergence failure with hundreds of gaseous and condensed species using models of nonideal mixtures of imperfect gases, compressible condensed species and liquid-solid and solid-solid phase transitions. The CERV method and code, based on reaction instead of composition variables, has inherent advantages mentioned earlier in achieving these goals. Although good methods and codes are available, computations are nonetheless limited by the scarcity of data for gaseous species (EOS for imperfect gases, mixing rules) and condensed species (EOS for thermal expansion and pressurized contraction).

Some closed-vessel or E-V problems were introduced and solved so that results could be presented to illustrate the effects of nonideal mixtures of perfect and imperfect gases and the effects of compressibility of condensed species on the equilibrium-mixture temperatures, pressures and compositions. The effects of compressible in contrast to incompressible condensed species on enhancing the mixture pressure from the predominant effect of thermal expansion over high-pressure material compression is interesting and reported herein for the first time. However, more data is required to address these issues more completely.

Two T-P problems were introduced to illustrate that the CERV method and code can simultaneously handle gaseous, liquid and solid species of the same substance with ease, whether a particular problem has a final equilibrium mixture that features only the solid species, only the liquid species, both gaseous and liquid species undergoing condensation, both liquid and solid species in a phase transition (melting), or two solid species in a phase transition (not demonstrated).

The capability of a computer code to readily solving T-P problems with multiple gaseous, liquid and solid species formed from the same substance is important to the solution of E-V or closed-vessel problems. The solution of an E-V problem is determined iteratively by repeatedly solving a T-P problem and systematically adjusting the mixture temperature while updating the mixture pressure based on the known closed-vessel volume at each iterative step until the final energy of the reaction products is equal to the initial energy of the reactants. Each new T-P problem should use the mole numbers of the previous T-P problem as initial guesses for computational efficiency during the iterative procedure. Because a previous solution may contain multiple gaseous, liquid and solid species formed from the same substance during condensation or melting, they need to be handled without difficulty or convergence failure in proceeding to the next iterative step. This is achieved easily by means of the CERV methodology (with reaction variables) and with a well-written CERV code.

The BNR methodology (with composition variables) in contrast has inherent difficulties in using mole numbers directly from an earlier iterative step when multiple liquid and solid species of the same substance are present, because matrix $\boldsymbol{A}$ can become singular theoretically or numerically with a convergence failure on inversion, unless some species are rejected from the mixture to make $\boldsymbol{A}$ invertible before proceeding.

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